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Isothermal Annealing and Relaxation of the Second Harmonic Generation Signal from a Nonlinear Optical Polymer

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Abstract

Results of the first detailed study of the effect of isothermal annealing on the relaxation behavior of the second harmonic generation signal below T_g of nonlinear optical (NLO) polymers are presented. Lengthening of the NLO chromophore relaxation time by isothermal poling suggests a strategy for preparing a stable NLO material.

To prepare a polymeric second harmonic generation (SHG) material, one needs to deal with the effect of thermal annealing in order to enhance the ultimate electric field employed to polarize the nonlinear optical (NLO) chromophores which are incorporated in the polymer. The NLO response of the polymeric SHG material is determined mainly by the behavior of the electric field induced polar orientational order parameters (POP), $<P_1(\cos\theta)>$ and $<P_3(\cos\theta)>$.[1] Here θ is the angle between the dominant principal axis of the molecular hyperpolarizability tensor and the poling field; $P_1(x)$ and $P_3(x)$ are the Legendre polynomials of order 1 and 3, respectively; the angular brackets denote an ensemble average. At low chromophore concentration where the anisotropic intermolecular interaction involving the NLO chromophore can be neglected, the POPs can be calculated from the Langevin functions. However, the orientational pair correlation needs to be considered at greater chromophore concentrations where the dipole-dipole interaction becomes comparable to the electric field-dipole interaction energy.[2]

After poling polymer chain motion in response to isothermal annealing plays a dominant role in affecting the stability of the SHG signal. However, the relaxation behavior of the SHG signal in regard to poling and polymer chain motion is not presently understood. In this communication we present results of the first detailed study of the effect of isothermal annealing on the relaxation behavior of the SHG signal below the glass transition temperature (T_g) of a NLO polymer. We show the effect of thermal cycling on the relaxation time of the POP.

The polymer chosen for the present study is a guest/host system involving a NLO chromophore 4-amino-4′-nitro-trans stilbene (NAS) dispersed in polymethyl methacrylate (PMMA). The guest/host system, rather than the main polymer, is preferred because of the ease in varying the concentration and short relaxation times. A set of samples with different NAS concentration were prepared. The glass transition temperature (T_g) of each sample was

determined by using a DSC (Perkin Elmer delta series). The T_g of the NAS/PMMA sample decreases steadily with increasing the NAS content. For pure PMMA, it is 119°C and it decreases to 110°C at 5 wt% NAS concentration. To carry out the SHG study, the NAS/PMMA samples were dissolved in chloroform and spin coated on electrically conducting glass slides (indium tin oxide coated on soda lime glass slides). The thickness and refractive index of each NLO polymer film were determined by the waveguiding technique. The NLO polymer was polarized using a contact electrode poling technique. The SHG experiments were carried out by using a Nd:Yag laser at 1.06 μm served as the fundamental beam. The SHG intensity at 532 nm was found to be proportional to the square of the strength of the poling field. Under a fixed poling field, the SHG signal remains constant even when the temperature was varied from 10° below to 50°C above T_g, in contrast to the corona poled main chain polymer in which a strong temperature dependence was observed.[3]

Upon removing the poling field, the SHG signal starts to decay. The decay of the SHG signal reflects the reorientational process by which the chromophore orientational alignment relaxes to thermodynamic equilibrium. In other words, the decay of the SHG signal reflects the relaxation behavior of $<P_1(\cos\theta)>$ and $<P_3(\cos\theta)>$ induced by the external electric field. However, shown in ref. 2, in the weak field poling condition, the $<P_3(\cos\theta)>$ order parameter is not induced, and the decay of the SHG intensity reflects the relaxation behavior of $<P_1(\cos\theta)>$

Shown in Fig. 2 is a series of isothermal SHG intensity relaxation waves for the 5 wt% NAS sample (T_g = 110°C) repeatedly poled at 100°C (10°C below T_g) under a constant electric field of 112.9 V/μm. One notes in (a) of Fig. 2 that the SHG signal decays rapidly in about 50 seconds. After the relaxation was completed, the sample was re-polarized under the same field strength; after the SHG intensity reached the same magnitude, the poling field was then removed, and the relaxation curve was monitored. This cyclic

poling/relaxation experiments were repeated, and monitored. As clearly shown in Fig. 1, the relaxation curve gradually lengthens after each cycle. The relaxation time starting from less than 50 s (curve a) and reaching more than 2000 s (curve h) after 8 cycles.

As found in previous studies,[4-6] the SHG intensity could be fit satisfactorily to a two-exponential model

$$I_{SHG} = (ae^{-(t/\tau_1)^{\beta_1}} + be^{-(t/\tau_2)^{\beta_2}}) \quad (1)$$

where τ_1 and τ_2 are the relaxation times associated with short and long decays, respectively. The amplitude of the short time decay was found sensitively dependent on the annealing time and the poling field. Shown in Fig. 2 are two curves obtained for the sample containing 5 wt% NAS poled at 110°C under the field of 72.6 and 91.8 V/μm, respectively. In Fig. 2(A), a large short time decay was observed; the rapid decay diminished, however, when the sample was poled under a larger field (Fig. 2B). The short time decay probably involves facile chromophore reorientation in the region with high local free volume which was annealed away isothermally or was decreased due to electrostriction under a high poling field. Our data also show that the relaxation time τ_2 is increased with increasing poling time (Fig. 3). The lengthening of the relaxation time with increasing poling time suggests that the SHG signal is stabilized by the increase in the polar orientational order parameter, a result consistent with a recent calculation based upon the orientational pair correlation model.[2,7] One further notes the fact that effective poling can be carried out below T_g suggests the importance of secondary relaxation processes in achieving alignment and orientational relaxation of the NLO chromophores.

The observation of the increase in the relaxation time τ_2 suggests that the stability of the SHG response can be achieved by subject the NLO film under an isothermal poling

condition. It is well known that isothermal annealing below T_g causes volume contraction.[8] As a result of physical aging the available free volume for reorientation of chromophores diminishes under isothermal annealing. Rapid reorientation of the NLO chromophores due to poling above T_g and followed by isothermal annealing below T_g thus provides an effective strategy for preparing a stable polymeric SHG material.

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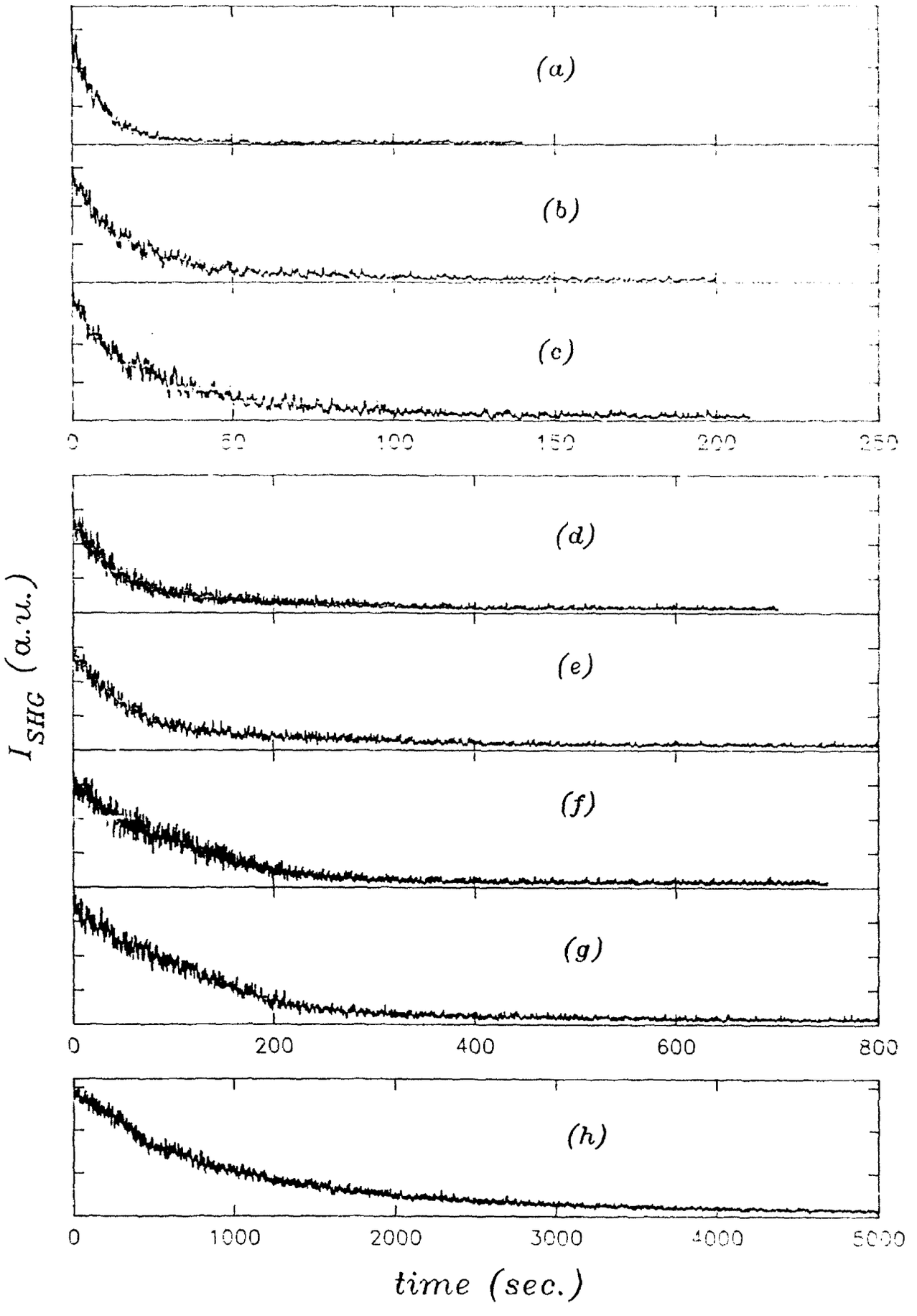
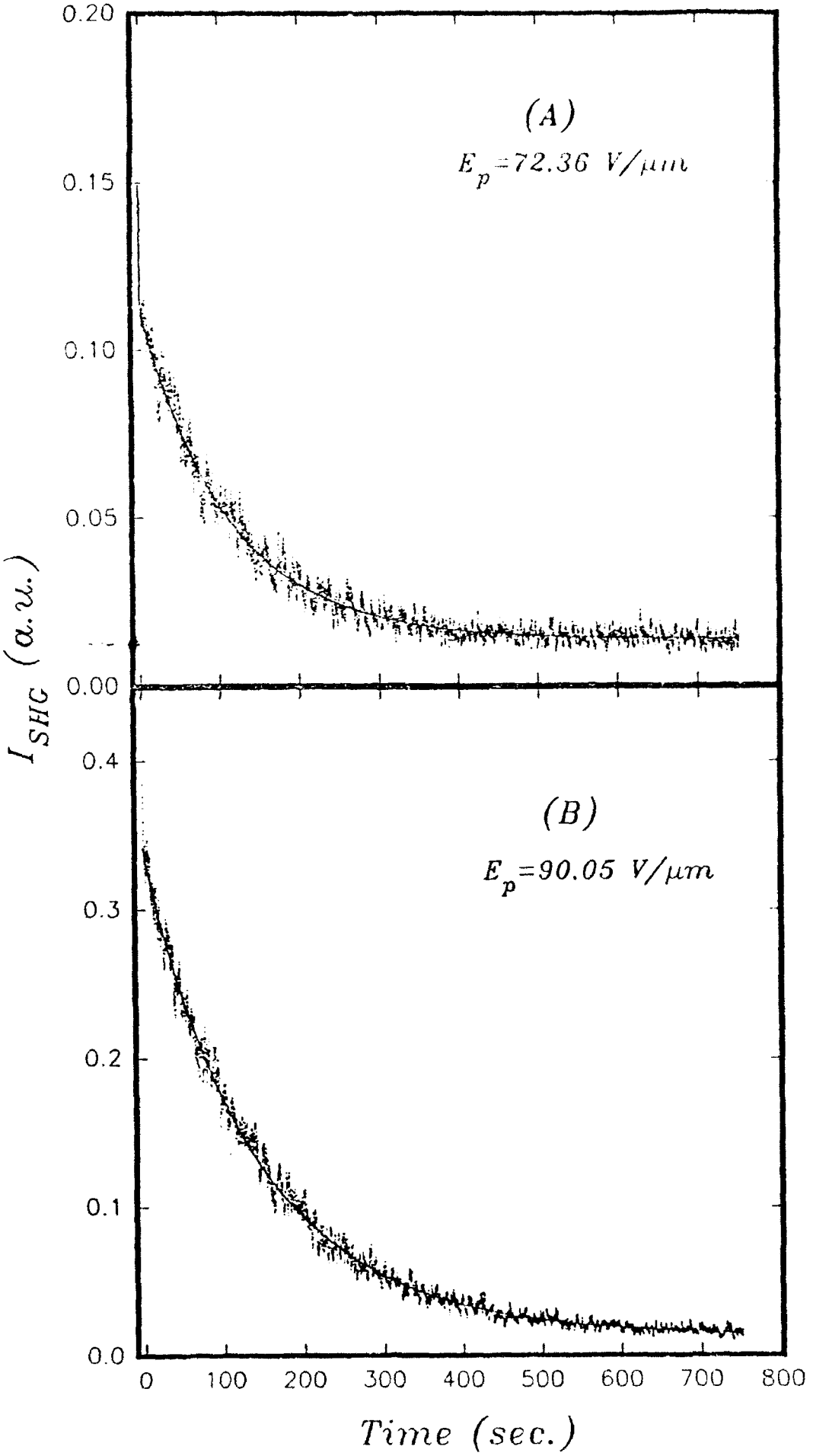
Figure Captions

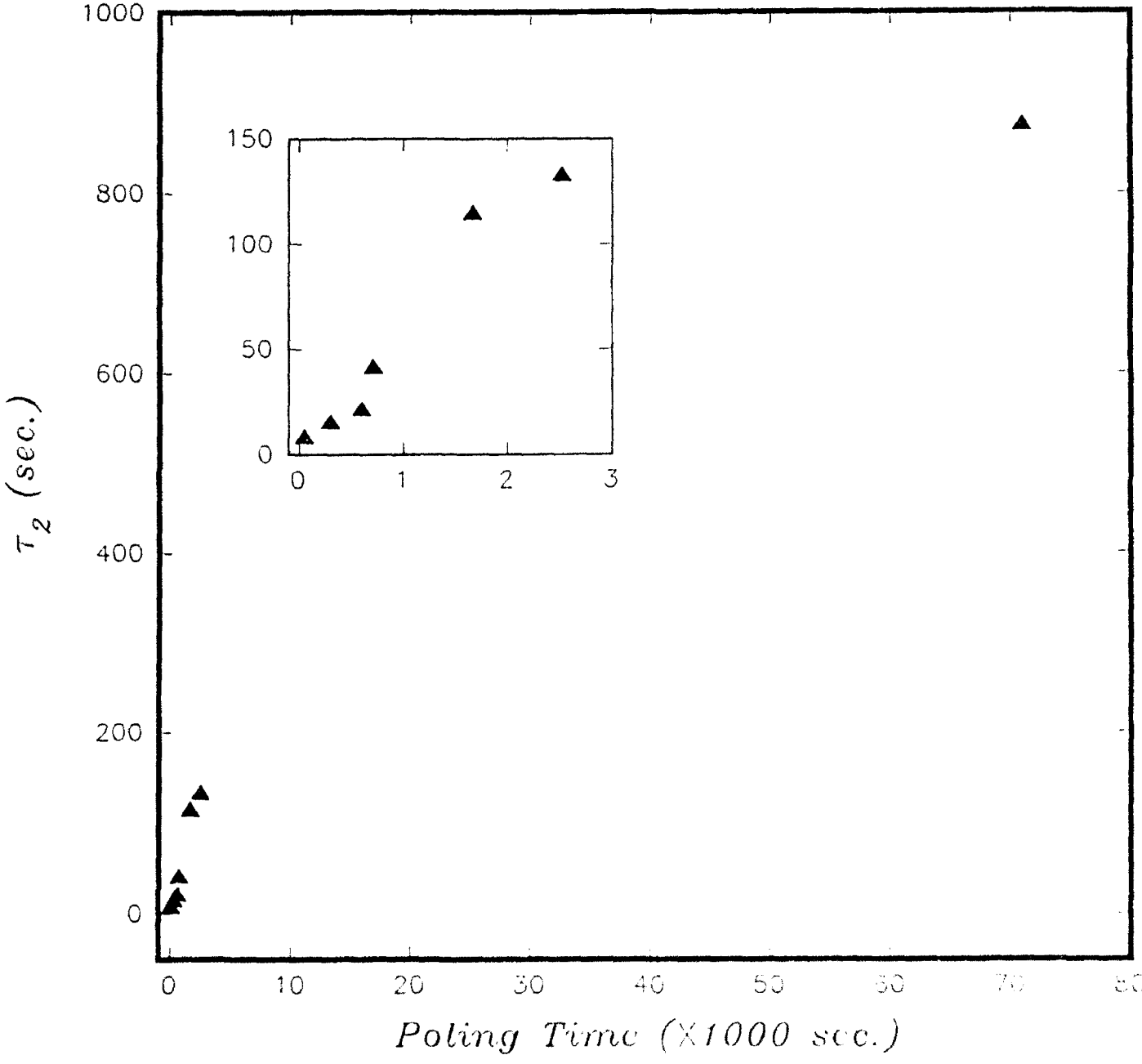
Figure 1 SHG intensity relaxation curves obtained under an isothermal condition (at 100°C) and poled at a fixed field strength of 112.9 V/μm. Curves from top to bottom represent successive cyclic poling/relaxation measurements made on the same sample.

Figure 2 SHG intensity relaxation curves obtained for the 5 wt% sample poled at 110°C under two different field strengths. Note the greatly reduced short time decay complitude for the curve poled at a higher field.

Figure 3 Relaxation time τ_2 obtained from the long-time decay curve plotted versus poling time under the isothermal condition.


(a)
(b)
(c)
0
50
100
150
200
250
(d)
(e)
(f)
(g)
0
200
400
600
800
(h)
0
1000
2000
3000
4000
5000
I_{SHG} (a.u.)
time (sec.)


(A)
E_p=72.36 V/μm
(B)
E_p=90.05 V/μm
I_{SHG} (a.u.)
Time (sec.)
0.20
0.15
0.10
0.05
0.00
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800


1000
800
600
400
200
0
τ_2 (sec.)
0
10
20
30
40
50
60
70
80
Poling Time (X1000 sec.)
150
100
50
0
0
1
2
3